Total Nitrogen Analysis by Combustion

1. Scope:

To provide a standardized procedure for the analysis of total nitrogen in fertilizer using the Dumas combustion method.

2. Principle:

Samples are prepared according to Sample Preparation, Storage, and Disposal (RA-SP-SMPL-PREP). Samples are combusted at high temperature (~1000°C) with high purity oxygen. This releases gaseous substances such as carbon dioxide, water vapor, and nitrogen oxides. The gas mixture passes over hot copper using helium to remove any residual oxygen and convert nitrogen oxides into molecular nitrogen (N_2). The mixture then passes through traps that remove water vapor and carbon dioxide. The amount of N_2 is quantified using a thermal conductivity detector. A 1:1 ratio of sucrose:sample is used to aid in combustion.

3. Safety:

3.1. All laboratory safety rules for chemical handling, sample preparation, and analysis shall be followed. Read the SDS for all materials before use.

3.2. The Rapid MAX N Exceed is a high temperature combustion analyzer. Refer to the Rapid MAX N Exceed instruction manual for specific warnings.

3.3. Ethylenediamine tetraacetic acid (EDTA) is a severe eye, skin, and respiratory system irritant. Dispense in a fume hood. Wear personal protective equipment and avoid all contact and inhalation of this material.

3.4. Compressed gas cylinders present a variety of hazards. Mandatory training is required before cylinders are transported, connected, or dispensed. Perform leak tests after connecting the oxygen and helium tanks to the Rapid MAX N Exceed.

4. Equipment (equivalents are acceptable):

4.1. Nitrogen combustion analyzer (Elementar Rapid MAX N Exceed)
4.2. Analytical balance (Mettler Toledo XS 204)
4.3. Oven (Fisher Scientific Isotemp Oven 725°F)
4.4. Desiccator

5. Reagents and Supplies (equivalents are acceptable):

5.1. EDTA (Ethylenediamine tetraacetic acid, CAS #6381-92-6, Alpha Resources #AR2092)

5.2. Aspartic Acid (CAS #56-84-8, Sigma #A9256)
5.3. Helium (Minimum 99.996% purity)
5.4. Oxygen (Minimum 99.998% purity)
5.5. Refer to the instrument manual for other reagents and supplies.

6. Instrument Preparation:

6.1. Verify the intake pressure at the delivery point is 2.5 bar for oxygen and 3.8 bar for helium.

6.2. Verify all parameters meet the instrument's setting value (all should be green).

6.3. Verify the instrument maintenance intervals and perform any necessary maintenance.

6.4. Perform oxygen and helium leak checks by selecting Diagnostics | Leak Check then Options | Diagnostics | Leak test. Follow the instructions given (close oxygen supply at the tank and reduce carrier-gas (helium) pressure at the tank to 1.5 bar). If the leak test does not pass, follow the instructions to locate and fix the leak. The leak test components kit is required for this operation.

6.5. Perform the following steps each day before analyzing samples. These steps include determination of instrument blank values, instrument conditioning, and determination of daily factor.

6.5.1. Select Options | Setting | Methods and select the appropriate method.

6.5.2. The software highlights which sample is being currently run in green. Yellow indicates which sample is currently being weighed. The red "stop" tag indicates after which sample the instrument will stop the run.

6.5.3. Run one empty sample without a crucible with 1.0 in the "Weight [mg]" column and "blank" in the method column to check for blockages and to verify the reductor tube is viable. If the blank N Area value is above 150, run another blank. If it is still above 150 run a third blank. If it is still above 150, investigate the reason as instrument maintenance may be required.

6.5.4. To determine instrument blank values, run three empty sample crucibles with 1.0 in the "Weight [mg]" column and "blank[O_2]" in method column. The first blank N integral value may be high after prolonged breaks between measurements or after maintenance. After stabilization the blank N integral values should be less than 150 units. If the first blank is high, run additional blanks until 3 consecutive values are below 150 units.

6.5.5. To condition the instrument, run two ~250mg aspartic acid standards as "Run-In" samples. Select the appropriate method according to the sample amount.

6.5.6. Run three aspartic acid standards (~150mg) using the same method as 6.5.5 to determine the daily factor.

6.5.7. Run an EDTA check standard (~150mg fertilizer with NO sucrose added) using the same method as 6.5.5. The acceptable result is within 1.5% of the

theoretical value (9.56 for EDTA). If the check standard fails, it may be rerun. If it passes then proceed with analyzing samples. If it still fails, perform step 6.5.6 again and rerun the check standard. If it continues to fail, instrument maintenance may be required.

7. Analysis

7.1. Enter sample names in the operating software and choose a method for each sample. Method “aspartic acid 1” is for 0 to 150mg of sample. Method “aspartic acid 2” is for 150 to 600mg of sample.

7.2. Thoroughly mix the sample before weighing by rotating the jar for solid samples or by shaking the bottle for liquid samples.

7.3. Tare an empty steel sample crucible and weigh ~150mg of sample (send the weight to the computer). Tare the balance, then add ~150mg sucrose into the same sample crucible. Insert the sample crucible on the appropriate position of the carousel.

7.4. Start the sample analysis by clicking the “Auto” (Green **II**) or “Single” (green **I**) button. “Single” runs the current sample and then stops. “Auto” runs all samples until the end or it reaches stop tag.

7.5. There are 2 ranges where area counts should fall. The lower range is 171 – 21,900 and the higher range is 21,901 – 385,451. Sample area counts should fall within one of these ranges. If it is outside these ranges or is close to one of the end points, the sample volume should be adjusted so it is within one of the ranges and is not close to the end points.

7.6. Any sample that fails to meet the guarantee shall be rerun. If a liquid sample fails to meet the guarantee twice and is basic (basicity can be verified using pH paper), 3 drops of acetic acid may be added to aid in the nitrogen recovery by preventing the release of NH_3 gas. Analysis using acetic acid should be repeated to verify consistent results.

7.7. A check or calibration standard (EDTA) shall be the last sample analyzed. One empty sample without a crucible may be run after the last standard to clean the machine with 1.0 in “Weight [mg]” column and “blank[O_2]” in method column.

7.8. When the last analysis is complete, print a report of all blanks, calibration standards, check standards, and samples run then set the instrument to sleep mode by selecting Options | Settings | Sleep/Wake-up.

8. QA/QC:

8.1. All check standards shall be within 1.5% of the theoretical value. If a check standard fails, it may be rerun. If it still fails, the daily factor determination shall be repeated, and the check standard run again.

8.2. The check standard is run after the daily factor determination and before samples to check the daily factor.

8.3. A check standard shall be analyzed at least after every 15 samples to check/maintain instrument calibration and shall also be the last sample analyzed (except for the cleaning sample, described in 7.6).

8.4. Any samples that are bracketed by an acceptable check standard result or calibration standard result are considered valid and may be reported.

8.5. The reporting limit (RL) is 0.02%.

8.6. The measurement uncertainty 0.3% for samples <1% nitrogen and 0.49% for samples ≥ 1% nitrogen.

9. Maintenance:

Maintenance	**Interval**
Instrument and supply lines leak test	Daily when instrument is used
Calibration (performed by manufacturer)	When the daily factor is no longer between 0.9 and 1.1. Manufacturer recommends every 10 years.
Checking/replacing the gripper arm	Visually inspect every day the instrument is used. Replace if there is buildup or the grooves have worn
Replace sealing elements (o-rings, quad rings, half shells)	Visually inspect and replace when visibly cracking or when leaking but no later than every year
Clean the carousel	When ash is present
Replace reaction tubes (combustion tubes/EAS-Reductor), replace fillings, check plugs and o-rings at the same time	See Options | Maintenance | Intervals in the operating software.
Check/replace drying tube(s), check o-rings at the same time	Daily visual inspection. Replace the drying tube when the blue color reaches ~3/4 the way to the top of the tube. Replace the absorption tube when it is white ~3/4 of the way to the top of the tube

10. References:

Operating instructions, rapid MAX N exceed analyzer, version 06.09.2017.

Approvals:

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Revision Log:

Date	What was Revised? Why?
1/29/21	Removed reference to crude protein. Added measurement uncertainty.
5/12/22	Changed calibration interval to 10 years based on manufacturer's recommendation. Added option to acidify basic samples. Minor wording changes to add clarification.